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(54) ELASTIC CROSS-LINKABLE FILAMENTS

(71) We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to elastic cross-linkable filaments.

Natural rubber thread is cheaper but has the severe disadvantages expected from its relatively high unsaturation. It is susceptible to damage by body oils, perspiration, light, laundering, flexing, etc.

In contrast, spandex elastic filaments (the word SPANDEX is a registered Trade Mark) are stronger (permitting the use of finer threads), are more resistant to oils, cleaning, etc., and can be used and dyed in the uncovered form. Their disadvantages include high cost, susceptibility to damage by bleaches, yellowing in light and on washing, weaving problems stemming from the presence of finishing oil on the thread, and loss of its superior strength and extension when heat set at 250° to 280°F.

Normally, elastomers are characterized by the fact that they have little or no crystallinity at rest although some of them crystallize upon elongation. Some of them have not had the requisite physical properties to be drawn into filaments. Further, filaments made from such elastomers have little strength and thus such elastomers have been of limited interest since they lack most of the fundamental characteristics known to be minimally necessary for a fiber.

It has been found that certain elastomers having a certain crystallinity range at rest and a certain green strength can be spun

into excellent elastomeric filaments; the ability of an elastomer to perform satisfactorily being related to its green strength, the degree of crystallinity of the elastomer being only one component albeit a vital one of several which in their totality result in the requisite green strength. Green strength is defined in greater detail later herein but briefly, it is a measure of the strength of the unvulcanized elastomer.

It has long been known that natural rubber and some synthetic elastomers of low or no crystallinity at rest are crystallizable, that is, they can be oriented upon stretching to form crystalline regions. It has also been observed that those elastomers which crystallize on stretching have considerably higher tensile strength after stretching than the elastomers which do not exhibit such crystallizability. This additional strength which becomes available through stretch-induced crystallization is very desirable, where relatively small diameter filaments are to be formed from an unfilled elastomer, as the stresses on such an elastomeric filament are very considerable.

Thus, the induction of crystallinity in an elastomeric filament upon stretching provides crystallites which act as tie-points to prevent, or at least reduce the extent of viscous or irreversible deformation. In turn, since the stress-induced crystallites can melt on removal of the stress, elastic recovery from deformation is permitted. Also, as a result of the crystallites in the stretched elastomers acting as tie-points, the modulus of elasticity is increased by the stretching.

In addition, the forces that form crystal lattices within the rubber molecules are relatively weak and therefore, in many instances, should be supplemented by either additional transient crosslinks or vulcanized covalent bonds or hydrogen bonding.

[Price 25p]

Notwithstanding that an elastomer may have the ability to crystallize upon stretching, it must also have the ability to be pulled or stretched after the initial fiber is formed by spinning. This requires a relatively high tensile strength of the uncured elastomer which is conventionally referred to as green strength.

For example, natural rubber has a relatively good green strength and a relatively high degree of crystallizability upon stretching and can form and has formed, filaments which are usable. But these filaments have limitations because the high number of double bonds in the backbone of the elastomer are particularly susceptible to oxidation and garments or fabrics lose their holding power or elastic nature on prolonged use. For such uses as girdles, sock tops, or elastic bandages, this is undesirable.

Butyl rubber is also crystallizable upon stretching and is relatively resistant to oxidation as compared to natural rubber. However, commercial butyl rubber lacks green strength at normal ambient temperature and cannot without appropriate modification (i.e. very high molecular weight or a reduction in temperature) be conveniently pulled into filaments before it falls apart.

According to the present invention an elastic, cross-linkable filament (suitable for making into a yarn) of from 0.5 to 1,000 denier comprises an olefin polymer containing a major proportion of ethylene and at least one other C_3 to C_{10} alpha olefin, said polymer having a crystallinity at rest and a green strength each as hereafter defined. The alpha olefin copolymers can be composed of ethylene and one or more said alpha olefin monomers. They can be fully saturated or they can contain an unsaturated monomeric substituent, viz. 0.1 to 2.0 wt. % of a diolefin having 5 to 40 carbon atoms, for example alkylidene norbornene, a cyclopentadiene, a hexadiene or another of the diolefins hereinafter listed.

It is to be emphasized that the only polymers of the above class which are within the invention, are those which have a crystallinity at room temperature of 1 to 20%, preferably 2.5 to 15% and most preferably, 6 to 12%, measured at rest by x-rays before the elastomer has been stretched.

The filaments will usually be stretched during spinning at least about 1.5 times their length and preferably 2 to 8, most preferably 3 to 6 times the initial length. The stretching not only orients the crystallites already present in the elastomer but causes the formation of additional oriented crystallites, which adds to the strength of the elastic filament.

Furthermore, the elastomers within the purview of the invention have a green strength of from 200 to 525 psi, and prefer-

ably within the range of from 250 to 500 psi, and most preferably in the range of 300 to 450 psi, at normal ambient temperature.

Attention for the purposes of ready explanation will be focused on a particular highly specific but preferred embodiment which is a terpolymer of ethylene, propylene and a diolefin, and is prepared with a specific preferred catalyst system. This terpolymer is substantially saturated in that not more than 20 wt. % of diolefin is used.

This terpolymer has a green strength of about 250 to 400 psi; and a crystallinity of about 9%. It can be spun by conventional methods into a filament, stretched and cured under tension by a suitable technique, such as with SCl_2 vapors to produce an elastic filament which has similar and even improved properties in some respects as compared to spandex filaments (SPANDEX is a registered Trade Mark) but at considerably lesser cost.

Because of its chemical structure, this novel elastic fiber has superior aging characteristics, as compared to other elastomers. It has excellent resistance to water, oxidation bleaches and chemicals. It also has an advantage of a low specific gravity (0.9 vs. 1.2 for spandex (registered Trade Mark)), which means less weight per volume, and consequently greater fiber lengths per pound of filament of a given diameter. Also, the filament of the invention when spun from solution is flat in cross section instead of round, which gives it greater bulk for a given weight. If a round cross section is preferred, it can be melt spun. Furthermore, the properties of the filament of the invention can be changed to fit practically any need by changing the ethylene content, the unsaturation, the degree of crystallinity, or the molecular weight of the polymer or by modifying the spinning process or the curing process. Finally, its cost is low, roughly in the same range as the crimped or so-called stretch fibers.

In general, the green strength, i.e. tensile strength, before curing of this olefinic elastomer is related to the ethylene content. Thus, using the preferred catalyst system of the invention, polymers of satisfactory green strength can be prepared containing from 60 to 85 wt. % of ethylene, preferably 65 to 80, and most preferably about 68 to 78 wt. % ethylene. A preferred terpolymer comprises 60 to 85 wt. % ethylene, a C_3 to C_{10} alpha olefin and 0.1 to 20 wt. % of the said diolefin. For other catalyst systems, the ethylene content may vary considerably to achieve the requisite crystallinity and green strength but the elastomer will generally comprise at least a major proportion of ethylene.

Although any of a multitude of processes known to the art can be used for producing

such terpolymer, it has been found that very satisfactory results are achieved when using a catalyst obtained by reacting a selected vanadium compound with a selected titanium compound to get a reaction product which is believed to be a complex. The complex is subsequently activated by admixture with an aluminum alkyl compound. The resulting homogeneous catalyst is then used to copolymerize ethylene and a higher alpha olefin and the diolefin. It is to be emphasized that the diolefin can be omitted when certain cure systems, such as peroxides and other free radical techniques are to be used.

About 0.05 to 10 moles, preferably 0.15 to 1.5 moles of vanadium compound are reacted per mole of titanium compound; and about 0.05 to 1.0 mole, preferably 0.10 to 0.50 mole of the reaction product is utilized per mole of aluminum alkyl compound. The preferred catalyst for the particular polymer and the polymer so made is described in French Patent 1,560,567.

Other known catalyst systems, as disclosed in Canadian Patent 672,158, Netherlands Patent 229,984, or British Patent 927,604 are also useful.

It is to be emphasized that elastomers which do not have the requisite green strength as described herein will not be satisfactory for the purposes of making elastic fibers. In this application, the general term "fiber" includes filaments of 0.5 to 1,000 denier, which filaments can be used as such or made into yarn.

The range from 0.5 to 30 denier may also be referred to as micro-denier fibers. Fibers in the range of from about 100 to 1,000 denier are often referred to as monofil. Regardless of the particular terminology one wishes to employ, the important point is that elastic filaments in a very wide range of deniers can be prepared according to this invention.

Green strength of a polymer is a term which denotes the tensile strength of an elastomer before curing.

For the purposes of this invention, green strength means a reading in psi obtained on an elastomer which has been subjected to the following test. A 4 inch x 6 inch single cavity mold is preheated and then lubricated on both mold surfaces. Fifty-five grams of an uncured polymer containing (per hundred parts by weight of polymer) 200 parts by weight of SRF black and 100 parts by weight of extender oil (a paraffinic or aromatic hydrocarbon oil) and no other compounds, is placed in the mold with its grain lengthwise. The mold is placed in a Carver Press at 190°F. The platens are then closed and the load increased in three steps up to 24,000 lbs. within 45 seconds. The mold is held under pressure for an additional 75 seconds after which the heat is turned off

and water is circulated through the platens until they cool down to room temperature. The pressure is then released and the compound removed from the mold. The compounded pad is then relaxed for about 20 minutes at 25°C., after which the tensile strength is obtained using a Scott Tester and an extension rate of 20 inches/minute.

Green strengths of at least about 200—250 psi represent about the minimum amount that an elastomer can possess and still fit within the parameters defining a satisfactory fiber-producing elastomer.

It has been found that the green strength of elastomeric copolymers is related not only to the crystallinity of the polymer but in turn for many of the olefinic copolymers it is a function of the weight per cent of ethylene in the polymer. It is also very clearly a function of the molecular weight of the elastomer. Thus, copolymers prepared with the preferred catalyst system and containing about 72 wt. % of ethylene will have a green strength in the desirable range (i.e., about 250 psi or higher).

Copolymers containing about 73—74 wt. % of ethylene will have even higher green strengths (in the range of at least about 300). The green strength continues to rise with the proportion of ethylene in the copolymer, although when more than about 80 wt. % of ethylene is in the copolymer, other processing characteristics are not optimal. Thus, a copolymer with this high ethylene content has a high strength but low elongation. In other words, it is not an elastomeric material anymore. It is tending to become a crystalline thermoplastic filament similar to a polyethylene filament.

Conversely, if the filament is not crystalline enough, i.e., too rubbery, it will usually have a high elongation, but relatively low strength.

These considerations serve to emphasize the critical confluence of polymer properties which must be present in order to have satisfactory filament-producing elastomers.

The alpha olefin other than ethylene usable as the comonomer is a C₃ to C₁₀ alpha olefin which may be linear or branched if the branching occurs 3 or more carbon atoms from the double bond. And while a single olefin is preferable, mixtures of these C₃—C₁₀ olefins may be employed. Suitable examples of C₃—C₁₀ alpha olefins include: propylene, 1-butene, 1-pentene, 1-hexane, 1-heptene, 1-octene, 1-nonene, 1-decene, 4-methyl-1-pentene, 4-methyl-1-hexene, 5-methyl-1-hexene, 4,4-dimethyl-1-pentene, 4-methyl-1-heptene, 5-methyl-1-heptene, 6-methyl-1-heptene, 4,4-dimethyl-1-hexene, 5,6,6-trimethyl-1-heptene, 5,5-dimethyl-1-octene, and 5-methyl-1-nonene; particularly preferred herein, is propylene.

The diolefin is preferably nonconjugated

and if present is included in proportions of 0.1 to 20 wt. %, preferably 1 to 10 wt. %. It will have a carbon atom range of 5 to 40, preferably 5 to 20. Suitable diolefins include but are not limited to C_4 to C_{10} alkylidene norbornenes, such as 5-methylene-2-norbornene, 5-isopropenylnorbornene, 5-ethylidene-2-norbornene; dicyclopentadiene, 2-methyl norbornadiene, 4,7,8,9-tetrahydroindene, 1,5-cyclooctadiene, and 1,4-hexadiene. In this invention, 5-methylene-2-norbornene and 5-ethylidene-2-norbornene are preferred.

Although the specific embodiment herein is a substantially pure polymer, it is possible to blend various different polymers to achieve a resulting blend which possesses the requisite crystallinity and green strength to make an elastic filament according to the invention.

It is also possible to react the unsaturation in the polymer with a functional silane such as $HSiCl_3$, to produce functionality such as $-SiCl_3$, which can be moisture cured. Suitable processes for achieving this are described in U.K. Specification No. 1,167,521. By terpolymerization with a silane-containing monomer one can also get such polymers.

The vanadium compound which is used in the preferred process is either of a vanadium oxyhalide, a vanadium oxyacetylacetonate or alkyl vanadate. The vanadium oxyhalide has the formula VOX , wherein X is a halogen having an atomic number of more than 17, i.e., chlorine, bromine, or iodine. The preferred vanadium oxytrihalide is $VOCl_3$.

The vanadium oxyacetylacetonate has the formula VOA_2 , where A is the acetylacetonate radical or a haloacetylacetonate radical, the halogen being any of chlorine, bromine, iodine or fluorine. Examples of these compounds include vanadium oxydiacetylacetonate, vanadium oxy bis (dihaloacetylacetonate), and vanadium oxy bis (tetrahaloacetylacetonate). Preferred of this group is vanadium oxybisacetylacetonate.

The alkyl vanadate has the formula $VO(OR)_3$, wherein R is a C_1-C_{12} alkyl group, preferably a C_2-C_6 alkyl group. Examples of alkyl vanadates are $VO(OCH_3)_3$, $VO(OC_2H_5)_3$, $VO(OC_4H_9)_3$, and $VO(OC_8H_{17})_3$. The preferred alkyl vanadate is $VO(OC_2H_5)_3$.

The titanium compounds for this process have the general formula $Ti(OR)_4$, where R is a C_1-C_{12} alkyl radical. Preferably, R is a C_2-C_6 alkyl radical. Thus, R may be a methyl, propyl, butyl, pentyl, isopentyl, octyl, or hexyl group. Most preferably, R is a butyl group so that tetrabutyl titanate is the most preferred titanium compound.

The alkyl aluminum compound which is useful in this process has the formula R_mAlX_n , wherein R is a C_1-C_{12} monovalent hydrocarbon radical, X is a halogen having

an atomic number above 17 (i.e. Cl, Br, or I) or a C_1-C_{12} monovalent hydrocarbon radical, m is an integer between 1 and 3 inclusive, and the sum of m plus n is equal to 3.

Specific examples of R and/or X groups include methyl, ethyl, propyl, *n*-butyl, *n*-amyl, iso-amyl, phenyl, tolyl, and cyclopentyl radicals. Preferred are the C_1-C_3 alkyl groups such as ethyl and butyl groups. Most preferred is ethyl. The preferred halogen is chlorine.

Examples of suitable alkyl aluminum compounds include triethyl aluminum, tripropyl aluminum, diethyl aluminum chloride, and ethyl aluminum dichloride. Most preferred is diethyl aluminum chloride. Mixtures of alkyl aluminum compounds can also be suitably used.

In preparing and using catalysts according to this process, all steps should be carried out in the absence of oxygen, moisture, carbon dioxide or other harmful impurities. This end is readily accomplished by blanketing all of the raw materials including the catalyst components, monomers, and inert diluents with an inert gas such as dry nitrogen or argon. Preferably, all materials are purified, e.g., by drying, distillation, etc., prior to their use. The reaction temperature for the formation of the vanadium compound-titanium compound catalyst component is suitably room temperature. This temperature is not critical, however, and either lower temperatures (e.g., 45°F.) or higher temperatures (e.g., 100°F.) may be used, although in selecting a higher temperature, a factor to be considered is that the reaction is exothermic.

The conditions at which the polymerization reaction is carried out can vary over a wide range. Generally, temperatures ranging from -40° to $150^\circ C$. can be used; however, temperatures ranging from 0° to $60^\circ C$. are preferred. Pressures ranging from 0.2 to 1000 psig can be employed in the polymerization reaction; however, pressures in the range of from about 1 atmosphere to 10 atmospheres are more generally used. The reaction times used in the formation of the copolymers depend in general upon the temperatures used. Generally, reaction times ranging from 1 minute to 5 hours can be employed; however, it is more usual to use reaction times ranging from 5 to 60 minutes.

The reaction vessel can be constructed of any material that is inert to the reactants and diluents used, and is capable of withstanding the operating pressures. Reaction vessels made of glass, stainless steel and glass-lined steel are quite satisfactory. Details of the polymerization process have been generally described in the art; see for example U.S. Patent Specification 3,438,951.

Generally, the elastomeric copolymers will have a molecular weight in the range of

50,000 to 1,000,000 preferably 100,000 to 500,000, as determined by intrinsic viscosity in decalin solution at 135°C.

Various solvents may be used in the preferred embodiment of the polymerization process and they include aliphatic, naphthenic, aromatic and halogenated hydrocarbon solvents, or an excess of the higher alpha olefin such as propylene may be used. Examples of solvents include n-hexane, propane, cyclohexane, toluene, xylenes, tetrachloroethylene, decalin chlorobenzenes and methylchloride.

It is one of the outstanding features of the preferred copolymer of the invention that all of the normal means of filament spinning can be used including wet, dry, latex and melt.

It is a particular advantage that the suitable elastomers of the invention may be melt spun, since other elastomers tend to degrade at high melt spinning temperatures.

In these spinning processes a viscous fluid is extruded through a die or spinneret, preferably, multiholed to form a fiber. However, on a laboratory scale, it is preferable to just pull a filament from the melt or solution or extrude through a hypodermic needle.

The extruded filament may simply be cooled from melt temperature by ambient air or be exposed to a liquid or gaseous setting medium, such as a polar nonsolvent, e.g. an alcohol, ketone, or ester, although other classes of compounds such as amides, sulfides, amines, ethers, etc. are not excluded. Particularly advantageous are such low molecular weight ketones as acetone and 2-butanone and alcohols, such as methanol, ethanol, isopropanol, or butanol or mixtures thereof.

The elastomer may also be spun from a solvent cement, such as a solution of the elastomer in a wholly or predominantly hydrocarbon solvent, such as pentane, hexane, heptane, benzene, toluene, xylene, cyclohexane, methylcyclohexane. A de-ashed cement directly from the polymerization process could also be used. The term "de-ashed" means substantially free from inorganic catalyst residues from the polymerization process.

The cement concentration may be varied to give desirable handling properties or production rates; a suitable range is from 1 to 20 grams of polymer per 100 ml. of solvent and preferably 5 to 15 g./100 ml. It may be desirable to purify the polymer cement before spinning, such as by passing it through a resin column or by filtration.

The cement is extruded through a spinneret and then may be drawn into warm air or an evaporative atmosphere to remove solvent (dry spinning) or passed into a nonsolvent for the polymer to remove solvent (wet spinning). Suitable non-solvents are those listed above as setting mediums. Once

the filament is coagulated from wet spinning, which takes place any time from 5 seconds to 2 minutes after immersion in the nonsolvent, preferably about 20 to 90 seconds, it is removed from the nonsolvent and stretched to approximately one and a half to 10 times its length and preferably 2 to 8 times its length, and allowed to dry under tension. The same amount of stretching is performed on a filament during melt spinning or dry spinning.

The conditions of stretching and drying can be varied as will be apparent to one skilled in the art. The key is to pick a stretching factor which will allow crystalline orientation which gives the fiber its strength. Generally, the greater the stretching, the stronger the filament.

The choice of curing techniques will be largely dependent on whether the elastomer is saturated or unsaturated. If saturated or unsaturated, it can be cured with free radical curatives such as peroxides or radiation. See Brenner, "Commercial Implications of Radiation Processing of Plastics", pages 116-120 in Vol. 45, No. 8, April 1968 *Modern Plastics*. Microwaves can be used in lieu of thermal heating when the curing takes place through peroxide reactions.

For unsaturated elastomeric filaments sophisticated and quite novel curing techniques have been developed. It is to be emphasized that one of the important aspects of the invention is the fluid phase curing technique which can be utilized not only for the particular fiber forming elastomer described herein, but for any elastomeric uncured fiber containing unsaturation.

The preferred embodiment of the fluid curing approach can be carried out with any material which is normally gaseous, or can be made gaseous at ambient or slightly elevated temperatures, for example, up to 100°C., and is known to effect crosslinking of polymers with unsaturation. A particularly preferred material and one that has been used in the examples of the invention is sulfur dichloride, SCl_2 . Sulfur monochloride, S_2Cl_2 , or mixtures with SCl_2 may also be used although S_2Cl_2 reacts more slowly than SCl_2 . Also, organo-bis (sulfenyl-halide) compounds of the type ClS-R-SCl where R is an organic molecular (aryl or aliphatic or arylaliphatic) having from 1 to 50, preferably 1 to 10, and most preferably, 1 to 5 carbon atoms which can be substituted with either polar or non-polar substituents could also be used.

Trichloromethyl sulfenyl chloride, Cl_3CSCl , may also be used. This is unexpected because it only has one SCl group.

It has been additionally found and forms an optional feature of this invention, that when the SCl_2 is purified and the subsequent curing is effected in the absence of light,

the resultant cured filament is less likely to turn yellow when it is subsequently exposed to light.

Commercially available SCl_2 is an equilibrium mixture containing about 10 wt. % S_2Cl_2 and 5 wt. % Cl_2 . Rosser and Whitt, *J. Appl. Chem.*, 10, 229 (1960), have shown that this equilibrium can be displaced towards SCl_2 by destroying the equilibrium catalysts with 0.1% PCl_5 .

Also the bromine and iodine analogs of the chlorine compounds mentioned above can be used. It is essential that the curing reaction be rapid, but the properties desired in the cured filament will determine the final choice of curing agent.

The curing reaction may be carried out by exposure of the spun, extended filament to the vapors of the curing agent or to a solution of the curing agent in a nonreactive non-solvent for the polymer, e.g., a dilute solution of SCl_2 in CH_2Cl_2 . The concentration of the curing agent in solution or in the vapor phase is selected to give the desired rate and extent of cure. This will depend, for instance, on the temperature, the stress-strain properties desired from the finished fiber, the degree of unsaturation in the uncured filament, and the linear velocity of the filament passing through a curing zone or chamber in a continuous fiber production operation.

This invention is readily adaptable to a

continuous process, but if desired, the dried, spun filament may be stored before curing.

It will be understood that conventional and unconventional additives such as curatives, accelerators, fillers, extenders, plasticizers, other polymers, dyestuff modifiers, and the like, may be added to the elastomeric filament of the invention.

The invention will be further illustrated by the following examples.

EXAMPLE 1

A reaction product of VOCl_3 and tetra-butyltitanate was prepared by dissolving equal weights of VOCl_3 and $\text{Ti}(\text{O}-\text{butyl})_4$ in normal hexane to make a 1.0 g/100 ml catalyst solution. This formed a homogeneous solution and was accompanied by a significant heat effect apparently due to the formation of a new complex species. The reaction product was added to the reactor separately but simultaneously with 0.096 moles of aluminum diethylchloride and used to polymerize a mixture of ethylene, propylene, and 5 methylene-2-norbornene (MNB) in a liquid volume ratio of 1.0/1.0/0.03. The reaction conditions, the compositions of the polymer obtained and the physical characteristics of the resulting elastomers after being conventionally compounded with FEF black and a conventional hydrocarbon extender oil are shown in Table I.

TABLE I

Run No.	1	2	3
Temperature, °C.	35	26.5	15
Ethylene, Wt. %	74.6	75.3	72.9
MNB, Wt. %	2.7	2.7	2.6
Propylene Wt. %	12.7	12.0	14.5
FEF black/Oil (each in parts wt. per 100 parts wt. of elastomer)	200/100	200/100	200/100
Melt Extrusion Rate, Inches/Minutes	95	85	75
Mooney Scorch at 270°F., T ₁	12.8	10.9	11.3
Mooney Plasticity at 212°F.	92	106	106
Green Strength, psi	320	370	270

As can be seen from the bottom line of the Table above, these elastomers have very high green strengths. X-ray analysis showed the elastomers to have about 9% crystallinity.

EXAMPLE 2

Example 1 was repeated with the exception that 5-ethylidene-2-norbornene was substituted for the methylene norbornene. Equally good green strengths were obtained. X-ray analysis showed the product to have 9% crystallinity.

EXAMPLE 3

A solution of 9 wt. % in hexane of the

terpolymer produced by Example 1, was spun into a filament by extruding it through a hypodermic needle into an acetone bath. The filament was allowed to remain in the acetone for 30 seconds in order to set the surface. It was then removed from the acetone and stretched to approximately three times its length and allowed to air dry under tension. After drying it had a denier of about 200.

The filament, still under tension, was then cured by exposure to SCl_2 vapors (10 mole % SCl_2 in air). For purposes of subsequent comparison, other filaments were not cured.

Several characterizing tests were run on both cured and uncured filaments and the results were compared with literature values for spandex (Registered Trade Mark). These are summarized as follows in Table II.

TABLE II

	Spandex	Uncured Filament	SCl ₂ Cured Filament
Tenacity, g/denier	0.6—0.8	0.5—0.9	0.4—0.7
Tensile Strength, psi	7500—10,000	5500—8500	4500—7500
Elongation, %	500—600	600—700	100—200
Elastic Recovery, % ^(a)	95	95	95
Insolubles, % ^(b)	97	1	94

^(a) From about 90% of ultimate elongation.

^(b) After 48 hours in cyclohexane at room temperature.

It can be seen from the above data that the elastic filaments of the invention have properties comparable to those of spandex. The elongation of the cured product can be increased if desired by lowering the amount of unsaturation in the polymer, or by lowering the ethylene content, or by lowering the amount of stretch during drying or curing.

which follows, this is a very rapid curing technique and only short exposure times are necessary. However, after exposure the cured filament should be allowed to stand for at least 12 hours, preferably 24 hours.

TABLE III
SOLUTION CURING ELASTIC FILAMENT

Exposure Time Seconds ^(a)	Insolubles In Cyclohexane, %
0	15
2	86
4	84
6	80
10	80
30	82

^(a) Time immersed in 10 mole % SCl₂ in CH₂Cl₂.

EXAMPLE 4

A solution of 9 wt. % in toluene of the terpolymer produced by Example 2 was extruded continuously through a 0.063 inch spinneret into a coagulating bath of methanol. The extrusion rate was 3 feet per minute and residence time in the coagulating bath was about 1 minute. After leaving the coagulating bath, the filament was stretched to seven times its original length and then allowed to dry. The product was 200 denier and had a tenacity of 0.7 to 0.9 g/denier and an average elongation of 95%. The filament still under tension was subsequently cured by exposure to 10 mole % SCl₂ vapor in air for 3 minutes at 25°C. approx. The cured filament gave tenacities of 0.6 to 0.8 g/denier and elongations of 70—110% depending on the tension under which curing took place. Insolubles in cyclohexane were 90—93%.

EXAMPLE 5

The elastomer of Example 2 was spun into a filament by the technique of Example 4 and while still under tension was cured by immersion in a 10 mole % solution of SCl₂ in CH₂Cl₂. As can be seen from Table III

EXAMPLE 6

The elastomer of Example 2 was melt spun into a filament, stretched and cured while still under tension by exposure to radiation. Other elastomer filaments were prepared from an ethylene propylene copolymer (referred to in Table IV as "EPR"—ethylene/propylene rubber) containing 68% ethylene and with an intrinsic viscosity of 3.9 with no diene but with similar crystallinity; it was used to demonstrate the complete practicality of crosslinking a filament without the necessity of unsaturation.

The results with further details are summarized as follows in Table IV.

TABLE IV
RADIATION (COBALT 60) CURED ELASTIC FILAMENT

	Polymer	Compounding	Insolubles In Cyclohexane, %	
			Unradiated	Radiated In N ₂ ^(a)
5	Example 2	None	15 ^(b)	93
	Example 2	1 phr S*	42 ^(c)	96
	Example 2	1 phr S+2 phr Peroxide ^(d) ...	38 ^(c)	95
	EPR	None	35 ^(c)	74
	EPR	1 phr S	44 ^(c)	89
10	EPR	1 phr S+2 phr Peroxide ^(d) ...	35 ^(c)	87

^(a) 600 curies for 18 hours, 1 inch from source.

^(b) This filament wet spun—no exposure to elevated temperature.

^(c) These filaments were melt spun after heating to 190°C. Apparently some cross-linking occurred at this temperature.

^(d) Tertiary butyl hydroperoxide (90%).

* The expression "phr S" means parts by wt. Sulphur per hundred parts by wt. of elastomer.

EXAMPLE 7

Several elastomers with different crystallinity results were compared with literature values Table V.

TABLE V
COMPARISON OF CRYSTALLINITY WITH EASE OF MELT SPINNING

	Sample Designation	Crystallinity %	Wt. % Ethylene	Intrinsic Viscosity	Remarks
25	A	0	58	3.2	Couldn't spin—no Strength
	B	7	68	3.9	Spun easily
	C	9	74	3.1	Spun easily
	D	18	85	3.1	Spun with difficulty—low elongation

30 As can readily be seen from these data, crystallinity and ethylene content are important factors in filament spinnability according to this invention.

EXAMPLE 8

35 Into a 2.5 inches × 48 inches vertical glass tube plugged at the bottom was poured (dribbled down the sides) 1 ml. of SCl₂. The same was done in two similar glass tubes with

40 S₂Cl₂ and Cl₂CSCl. Four elastomeric filaments, prepared from the polymer described in Example 2, were then introduced into each of the tubes and exposed to the vapors for various times at room temperature. The extent of cure was determined after exposure by measuring insolubles in cyclohexane. The results obtained are summarized in Table VI as follows:

TABLE VI

50	Exposure Time Seconds	Insolubles, %		
		SCl ₂	S ₂ Cl ₂	Cl ₂ CSCl
55	5	90	—	—
	10	90	—	—
	30	91	20	21
	60	90	47	36
	120	—	64	41
	180	—	87	63

Although the Cl_2SCl was slow under the conditions used, the important and unexpected thing is that it worked at all. A more complete cure can be obtained by extending the time or raising the temperature.

EXAMPLE 9

PCl_5 was added to SCl_2 and nitrogen bubbled through until all the Cl_2 had been purged. The resultant partially purified SCl_2 was then used to cure filament prepared from the product described in Example 2. It was found to cure the filament faster and more completely than untreated SCl_2 .

WHAT WE CLAIM IS:—

1. An elastic, cross-linkable filament of from 0.5 to 1,000 denier comprising an olefin polymer containing a major proportion of ethylene and at least one other C_3 to C_{10} alpha olefin, said polymer having a crystallinity at rest of from 1 to 20% and a green strength (as hereinbefore defined) of from 200 to 525 psi at normal ambient temperature.
2. A filament according to claim 1 wherein said filament has been stretched sufficiently to cause orientation of crystallites thereby resulting in an increase in strength of said filament and an increase in crystallinity prior to cross-linking.
3. A filament according to claim 2 which has been subsequently cross-linked to at least a minor degree while being held under tension.
4. A filament according to any of claims 1 to 3 wherein said polymer contains 0.1 to 20 wt. % of a diolefin having from 5 to 40 carbon atoms.
5. A filament according to claim 3 wherein the cross-linking is accomplished by free-radical means.
6. A filament according to claim 4 wherein cross-linking is accomplished by fluid phase curing means.
7. A filament according to any of claims 1 to 6 wherein said polymer is a terpolymer comprising 60 to 85 wt. % ethylene, a C_3 to C_{10} alpha olefin and 0.1 to 20 wt. % of a diolefin having 5 to 40 carbon atoms.
8. A filament according to any of the preceding claims wherein the alpha olefin is propylene.
9. A filament according to any of the preceding claims wherein the diolefin is 5-ethylidene 2-norbornene.
10. A method of producing an elastomeric filament which comprises extruding an olefin polymer containing a major proportion of ethylene and at least one other C_3 to C_{10} alpha olefin, said polymer having a crystallinity at rest of from 1 to 20% and a green

strength (as hereinbefore defined) of 200 psi to 525 psi at normal ambient temperature, into a filament;

(a) allowing the surface of the filament to set;

(b) stretching the filament from 1.5 to 10 times its length;

(c) cross-linking the filament while under tension.

11. A method according to claim 10 wherein the filament is melt spun.

12. A method according to claim 10 wherein the filament is:

(a) wet-spun;

(b) the surface of the spun filament is allowed to set in a liquid setting medium;

(c) the spun filament is stretched from 1.5 to 10 times its length prior to drying;

(d) the spun filament is allowed to dry under tension;

(e) the filament is cross-linked while under tension.

13. A method according to claim 12 wherein the polymer contains 0.1 to 20 wt. % of a diolefin and is cured by exposure to a fluid cross-linking medium.

14. A method according to claim 13 wherein the fluid cross-linking medium is vaporous.

15. A method according to claim 13 or 14 wherein the fluid cross-linking medium is a compound of sulfur and chlorine.

16. A method according to any one of claims 12 to 15, wherein the liquid setting medium is a ketone or an alcohol.

17. A method according to claim 16, wherein the liquid setting medium is methanol, ethanol or mixtures thereof.

18. A method according to claim 15 wherein the cross-linking medium is SCl_2 vapor.

19. A method according to any one of claims 13 to 15, wherein the C_3 to C_{10} alpha olefin is propylene and said diolefin is ethylidene norbornene.

20. An elastic filament according to claim 1, substantially as herein described.

21. An elastic filament according to claim 1 substantially as described with reference to any of Examples 3 to 9.

22. A method of making an elastic filament according to claim 1 substantially as described with reference to any of Examples 3 to 6, 8 and 9.

23. A method of making an elastic filament according to claim 1 substantially as herein described.

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